Amine-Activated Iron Catalysis: Air- and Moisture-Stable Alkene and Alkyne Hydrofunctionalization

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Amine Activated Iron Catalysis: Air- and Moisture Stable Alkene and Alkyne Hydrofunctionalization

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Abstract. A simple alkyl amine ($^{i}Pr_2NEt$) has been used to activate an air- and moisture stable iron(II) pre-catalyst for alkene and alkyne hydrofunctionalization reactions. This amine activation has enabled the highly operationally simple hydrosilylation and hydroboration of alkenes and alkynes using just 0.25 - 2 mol% iron catalyst and 1 - 25 mol% amine. Significantly, these reactions proceed in equal yield under both air and inert reaction conditions.

Keywords: Hydrosilylation; Iron; Catalysis; Sustainable Chemistry

Following Speier's seminal development of the homogeneous platinum-catalyzed hydrosilylation of alkenes,[1] this transformation has become one of the largest industrial processes in current operation, due to the wide range of applications that use hydrosilylation products, for example silicon rubbers, molding products, release coatings, and pressure sensitive adhesives.[2,3] Although powerful, the current state-of-the-art catalytic processes rely on precious metal complexes (typically Pt or Rh), and are susceptible to unwanted side reactions such as dehydrogenative silylation and over-hydrosilylation to the tertiary silane.[2,4,5] More significantly, the homogeneous nature of these processes facilitates the loss of the precious metal by incorporation into the (polymeric) product.[6, 7] The majority of hydrosilylation products are dispersive polymers that make metal recovery and recycling extremely difficult. This is exemplified by the annual loss of 5.6 tons of Pt in hydrosilylation processes.[6]

Consequently, investigations into sustainable alternatives are paramount to future hydrosilylation procedures.[8,9] Chirik and co-workers have developed a series of formally iron(0) complexes which catalyse the *anti*-Markovnikov hydrosilylation of olefins with exceptional turnover frequency and turnover number (Fig. 1a).[6, 10-12] However, the Fe(0) (pre)-catalyst requires strictly air- and moisture-free environments for handling and use, thus limiting possible adoption, particularly on an industrial scale.[10]

The *in situ* activation of more robust Fe(II/III) precursors has emerged as a method to avoid the need to prepare and handle low oxidation-state species.[10,13] Strongly reducing organometallic reagents such as Grignard reagents,[13g,14] $NaHBEt_3$[13f,15,16] and activated magnesium[13d] are commonly used as activators (Fig. 1a). These reagents are inherently pyrophoric, unstable to both air and moisture, can be incompatible with substrate functionality, and negate the inherent environmental and practical benefits of using an iron (pre-)catalyst.

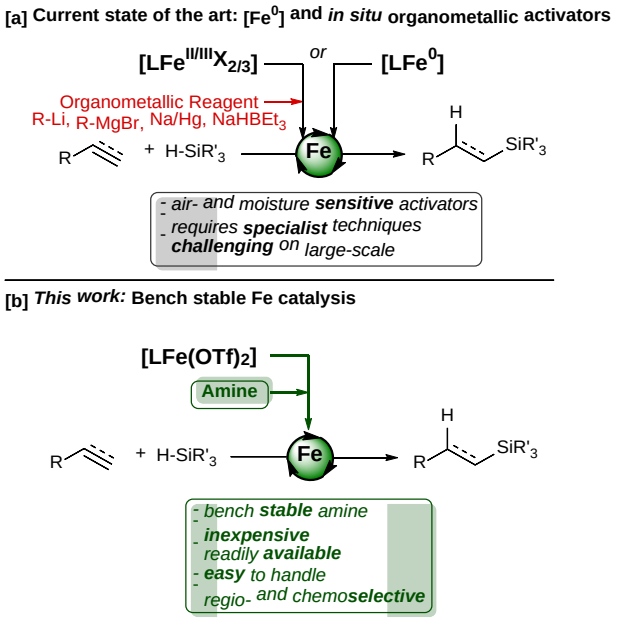


Figure 1. *In situ* activation methods, including this work. [a] Using organometallic reagents for pre-catalyst activation; [b] amine activation.

We sought to develop an iron-catalyzed hydrosilylation reaction that made use of inexpensive, readily available, and, importantly, easily handled reagents (particularly the activator and catalyst) that could be applied on a large-scale without the need for air- and moisture free techniques and reaction environments (Fig. 1b). Simple tertiary amines satisfy all of these requirements, and offer a novel mode of activation for iron catalysts. The use of amines to reduce metal pre-catalysts has been reported previously, but this is not known for the production of low oxidation-state iron species at room temperature.[17] In fact, the *in situ* activation of iron pre-catalysts has relied on reduction by organometallic reagents with a (conjugate acid) pK_a of above 36.[18]

Initial investigations focused on using simple amines to activate bis(imino)pyridine (BIP) Fe(II) pre-catalysts[9, 11] for the hydrosilylation of 1-octene (**2a**). The iron(II) chloride (**1a**) and bromide (**1b**) complexes showed no catalytic activity when using either triethylamine or di*iso*propylethylamine ($^{i}Pr_2NEt$) as the activator (Table 1, Entries 1-4). We postulated that the strong iron-halide bond prevented coordination of the amine to the pre-catalyst and therefore hindered any possible activation. We thus proposed that the use of a more weakly coordinating counter-ion could facilitate amine activation. The trifluoromethanesulfonate (triflate) counter-ion is significantly more labile than the halide counterparts, but yet imparts stability in the solid state.[19] Complexation of iron(II) triflate with the 2,6-bis[1-(2,6-diethylphenylimino)ethyl]pyridine (^{Et}BIP) ligand gave ^{Et}BIPFe(OTf)$_2$ (**1c**), an analogous pre-catalyst to the iron(II) halides, a purple mono-ligated high-spin Fe(II) complex. The single crystal X-ray structure revealed a coordinated aqua ligand,[19] and so revealed an accessible site for possible amine coordination (Fig. 2). Using pre-catalyst **1c** in the presence of both $^{i}Pr_2NEt$ and NEt_3 gave the linear hydrosilylation product **3a**, with complete control of regioselectivity and without any deleterious side-reactions such as dehydrogenative silylation,[20] over-hydrosilylation (to the tertiary silane product), hydrogenation or alkene isomerization (Entries 5 and 6). This promising result represents the first use of an amine to activate an iron (pre)-catalyst directly at room temperature, to the best of our knowledge, and greatly simplifies the practicality of low oxidation-state iron catalysis. Significantly, it was found that the presence of air had a negligible effect on catalyst activation and activity, and thus the use of Schlenk/air-free techniques were not necessary.[21] The use of organometallic reagents as activators for pre-catalyst **1c** led to reduced product yields compared to those using amine activation (Table SI.1; Supporting Information).[21]

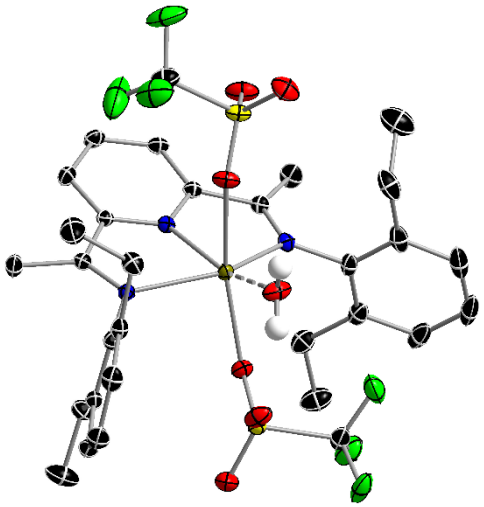
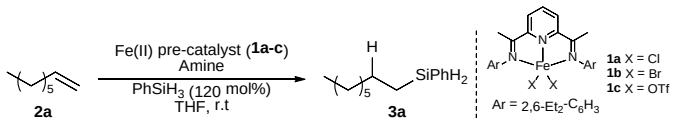


Figure 2. Molecular structure of ^{Et}BIPFe(OTf)$_2$ (1c). 50% probability of ellipsoids; Hydrogen atoms and solvent molecules omitted for clarity; Black = C, Blue = N, Red = O, White = H, Yellow = S, Green = F. CCDC 1452177 contains the supplementary crystallographic data for this paper. These

data are provided free of charge by The Cambridge Crystallographic Data Centre.

In a bid to increase the industrial relevance of this system, solvent-free conditions were investigated, and again the linear silane **3a** was produced (Entries 7 and 8).[7,22] Solvent-free reactions offer significant economic and environmental advantages by decreasing waste and avoiding the use of organic solvents. As $^{i}Pr_2NEt$ gave an excellent yield of product **3a** under these conditions, subsequent investigations were carried out using this amine. A reaction time of 1 hour or less was found to be sufficient for this reaction (Entry 9). Reducing the loading of $^{i}Pr_2NEt$ used to 25 mol% gave equal reactivity to that using stoichiometric amine (Entry 10). Even when the catalyst loading was reduced to 2 mol% an excellent yield and perfect regioselectivity was still achieved (Entry 11). Control experiments showed that both pre-catalyst **1c** and $^{i}Pr_2NEt$ were required for successful hydrosilylation (Table SI.2; Supporting Information).

Table 1. Initial Investigations and Reaction Optimization



Entry	Catalyst (mol%)	Amine (mol%)	Reaction Time (h)	Yield **3a** (mol%)[a]
1	**1a** (7)	$^{i}Pr_2NEt$ (120)	24	-
2	**1a** (7)	NEt_3 (120)	24	-
3	**1b** (7)	$^{i}Pr_2NEt$ (120)	24	-
4	**1b** (7)	NEt_3 (120)	24	-
5	**1c** (7)	$^{i}Pr_2NEt$ (120)	24	13
6	**1c** (7)	NEt_3 (120)	24	45
7[b]	**1c** (7)	$^{i}Pr_2NEt$ (120)	24	95
8[b]	**1c** (7)	NEt_3 (120)	24	43
9[b]	**1c** (7)	$^{i}Pr_2NEt$ (120)	1	87
10[b]	**1c** (7)	$^{i}Pr_2NEt$ (25)	1	80
11[b]	**1c** (2)	$^{i}Pr_2NEt$ (25)	1	95

[a] Yields determined by ^1H NMR spectroscopy, using a 1,3,5-trimethoxybenzene internal standard (20 mol%). [b] No solvent added.

The need for amine coordination to initiate pre-catalyst activation was confirmed by the addition of pyridine to a standard reaction [**1c** (2 mol%), $^{i}Pr_2NEt$ (25 mol%), pyridine (50 mol%)] resulting in greatly reduced catalyst activity (8% **3a** compared to 95% under standard reaction conditions, Scheme 1a).

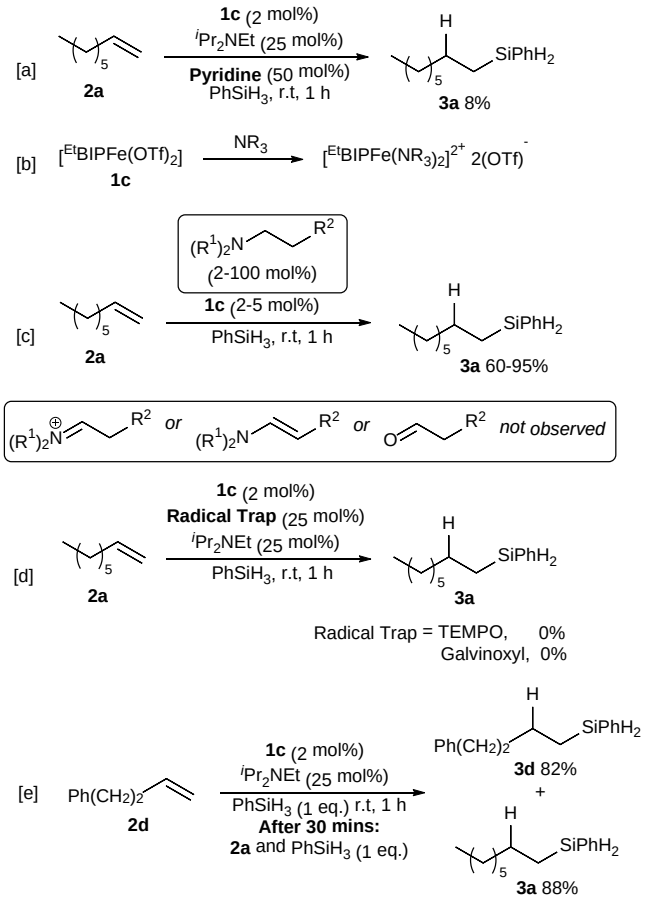
In order to further understand the mechanism of activation a series of stoichiometric reactions and NMR studies were carried out (See SI for full details). Amines are well known to reduce 2nd and 3rd row transition metal species by coordination and β–hydride elimination.[17a,b,h] A limited number of examples have also been proposed for iron species.[13b, 17d,e] Thus we initally focused on the observation of β-hydride elimination products from the amine activator; imine (or enamine, following tautomerisation) or aldehyde, following aqueous work-up.

^1H NMR and GC-MS studies of the reaction of amine and pre-catalyst **1c**, in the absence and presence of reactants, showed no observable formation of products arising from β-hydride elimination. In fact, the addition of $^{i}Pr_2NEt$ to pre-catalyst **1c** resulted solely in ligand exchange to generate the ligated Fe(II) bis-amine complex and free triflate, as confirmed by ^{19}F NMR (Figure SI.1). *N*,*N*-Dimethylbenzylamine was found to be an effective activator and offered the possibility of generating more stable β-hydride elimination products. Once again, no imine, enamine or aldehyde were observed using this amine activator (Scheme 1c, Table SI.3, Scheme SI.1)[17]. Further, 2,6-lutidene, which has no available β-hydrogens, was able to active pre-catalyst **1c**, albeit with low activity (Table SI.4). Thus, we propose that β-hydride elimination is not the mechanism of pre-catalyst activation, but a novel pathway is operating.

Although no reaction was observed for $Fe(OTf)_2$ or $^{Et}BIPFe(OTF)_2$ without amine, the addition of tetrabutylammoniumtriflate in place of amine confirmed that the triflate counter ion itself was not acting as the activator once dissociated (Table SI.5).[21] The use of triflate salts with benzylamine, an amine which displaces triflate from the pre-catalyst but does not initiate catalysis, also gave no hydrosilylation (Table SI.6).

As β-hydride elimnation was not detected, and free triflate was not active, we next considered a radical-type activation of the pre-catalyst. The exclusion of light and oxygen was not detrimental to activation or catalyst activity (Scheme SI.2). Tertiary amines have been shown to participate in single-electron transfer (SET) reactions, thus offering a mechanism for pre-catalyst activation.[23] However,

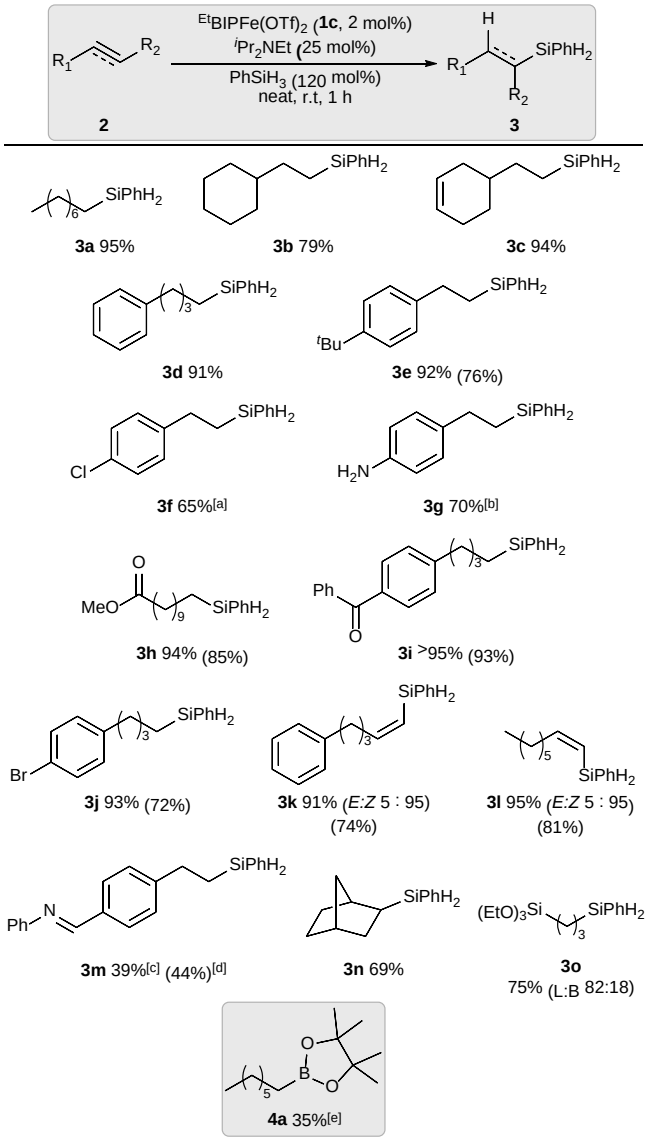
under no conditions could an amine radical cation be observed by EPR spectroscopy, although the short lifetime of trialkylamine radical cations may hinder detection. When 2,2,6,6-tetramethylpiperidin-1-yl)oxyl (TEMPO) was added to standard reaction conditions, catalytic activity deacreased with increasing stoichiometry of TEMPO until no activity was observed when the loading of TEMPO equalled that of amine (Scheme 1d). Catalytic activity could be regained by adding excess amine to a 'stalled' reaction (Table SI.7). The use of an alternative radical trap, Galvinoxyl, gave similar results. Therefore a radical activation mechanism is suggested.



Scheme 1. Summary of mechanistic investigations; [a] Pyridine addition hindered reactivity; [b] Displacement of triflate counter-ions by amine; [c] Attempts to recover amine by-products were unsuccessful, whilst primary amines do not activate this system [d] Addition of radical traps hinders reactivity; [e] Catalyst is still active upon completetion of hydrosilylation; see Supporting Information for further information.

To determine if catalyst decomposition was occurring under reaction conditions, an equivalent of 1-octene and phenylsilane were added to a standard reaction with 4-phenylbutene after 30 minutes. Both hydrosilylation products **3a** and **3d** were obtained in near-equal yield to that of the isolated hydrosilylation reactions (88% and 82% *vs*. 95% and 91% respectively), demonstrating that this catalyst is still active after hydrosilylation is complete (Scheme 1e).[21] Further mechanistic investigations are ongoing.

Table 2. Reaction Scope

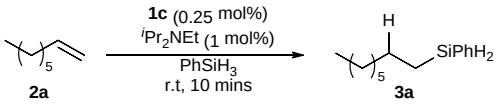


[a] ^{Et}BIPFe(OTf)$_2$ (4 mol%), 2 hour reaction. [b] ^{Et}BIPFe(OTf)$_2$ (3 mol%). [c] ^{Et}BIPFe(OTf)$_2$ (4 mol%), 18 hour reaction. [d] Recovered starting material. [e] pinacolborane (120 mol%), ^{Et}BIPFe(OTf)$_2$ (3 mol%), ^{i}Pr$_2$NEt (10 mol%). Yields determined by ^{1}H NMR spectroscopy using a 1,3,5-trimethoxybenzene internal standard (20 mol%), isolated yields are shown in parentheses.

The substrate scope and limitations of this novel hydrosilylation method were investigated. In all cases the highly efficient *anti*-Markovnikov hydrosilylation of terminal alkenes, to give linear silanes, was observed with complete control of regioselectivity and without any dehydrogenative silylation or over-hydrosilylation observed (Table 2). Aliphatic and aromatic alkenes underwent successful hydrosilylation to give the *anti*-Markovnikov silane (Table 2, **3a-d**). Chemoselective hydrosilylation of the terminal alkene of vinylcyclohexene (**2c**) was achieved without multiple hydrosilylation or alkene isomerization (**3c**). Styrene derivatives, including those bearing electron-donating and electron-withdrawing substituents, underwent successful hydrosilylation, again with complete control of regioselectivity (**3e-3g**). The chemoselective hydrosilylation of alkenes containing carbonyl functionalities was achieved without detriment to the regioselectivity for the linear silane, and with no reaction at either the ester or ketone groups observed (**3h-i**).[24] 1-Bromo-4-(3-butenyl)benzene (**2j**) underwent chemo- and regioselective hydrosilylation without any proto-dehalogenation observed.[25] High reactivity was observed using terminal alkynes to give the (*Z*)-vinylsilanes, again with excellent control of regio- and stereoselectivity, and, significantly, without hydrosilylation of the product alkene (**3k-l**).[13h] *N*-Phenyl-4-vinylbenzaldimine (**2m**) underwent the chemoselective hydrosilylation of the alkene in a moderate yield and without reduction of the imine, to give product **3m**. However, substrates bearing very strongly coordinating functionalities (e.g. nitrile and nitro groups) inhibited catalyst activity giving only recovered starting material (Table SI.8; Supporting Information).[21] This method was highly selective for terminal alkenes and alkynes, with internal alkenes giving significantly lesser yields (Table SI.9). However, norbornene, containing a strained internal alkene, underwent successful hydrosilylation in good yield (**3n**).

In order to demonstrate complimentary reactivity to current hydrosilylation manifolds and increase the industrial applicability of the hydrosilyation products prepared, the hydrosilylation of allyltriethoxysilane was carried out in good yield and regioselectivity using phenylsilane (**3o**). Unfortunately, the use of other silanes resulted in low reaction yield and catalyst activity. Amine activation was also found to be successful for the iron-catalyzed hydroboration of alkenes. Using pre-catalyst **1c** and pinacolborane (H-BPin) directly, the hydroboration of 1-octene was achieved, to give the linear boronic ester (**4a**).

1-Octene (**2a**) is a highly industrially relevant hydrosilylation exemplar, thus the limits of both catalyst and amine loading were investigated with this substrate (Table SI.10). Successful hydrosilylation was achieved using just 0.5 mol% pre-catalyst **1c** and 1.2 mol% $^{i}Pr_2NEt$ without any significant decrease to catalytic activity, regioselectivity or product yield (Table SI.10, Entry 1). In addition, an increase of $^{i}Pr_2NEt$ to 80 mol% had no effect on the hydrosilylation yield, allowing the amine to become the reaction solvent for solid substrates (Table SI.10, Entry 2). Importantly, and of industrial and practical relevance, the gram-scale hydrosilylation of 1-octene was complete within just 10 minutes, using only 0.25 mol% of catalyst **1c** under an atmosphere of air (Scheme 2). Equal reactivity in air and inert atmospheres were found for gram-scale reactions. This is a unique achievement in the field of low oxidation-state iron catalysis and one which paves the way for future exploitation by both the expert and non-expert alike. The pre-catalyst was found to be resistant to decomposition both in use and during storage 'on the bench', as aged pre-catalyst was found to still offer significant activity, again demonstrating the possibility of both this pre-catalyst and activation method to be used by the widest possible user base (Scheme SI.3).[21]



2a **3a**

2.2 g, 78% **air**[a]
8.5 g, 60% **air**[b]
8.3 g, 59% **inert**[b]

Scheme 2. Gram-scale hydrosilylation [a] Conditions: 1-octene (2 ml, 100 mol%), phenylsilane (110 mol%), ^{Et}BIPFe(OTf)$_2$ (0.25 mol%), $^{i}Pr_2NEt$ (1 mol%) complete in 10 mins under air, isolated yields reported. [b] Conditions: 1-octene (10 ml, 100 mol%), phenylsilane (110 mol%), ^{Et}BIPFe(OTf)$_2$ (0.5 mol%), $^{i}Pr_2NEt$ (4 mol%) complete in 10 mins under air or an inert (argon) atmosphere.

In summary, the highly operationally simple hydrofunctionalization of alkenes and alkynes has been developed using a bench-stable iron(II) pre-catalyst and *in situ* amine activator. Excellent reactivity,

chemoselectivity and complete control of regioselectivity has been achieved for a series of functionalized and unfunctionalized alkenes and alkynes and, significantly, the reaction was found to be unaffected by the presence of air. A catalyst loading of just 0.25 mol% was shown to be highly active in the hydrosilylation of 1-octene on gram-scale in only 10 minutes, under air, thus enabling the adoption of this catalytic manifold for more sustainable large-scale hydrosilylation applications.

Experimental Section

*Preparation of ^{Et}BIPFe(OTf)$_2$ (**1c**)*

Iron(II) trifluoromethanesulfonate and 2,6-bis-[1-(2,6-diethylphenylimino)ethyl]pyridine were stirred in THF for 16 hours. The solvent was then removed *in vacuo*. Diethyl ether was added and this mixture was stirred for a further 24 hours. The solvent was removed to provide an amorphous pink/purple solid. See Supporting Information for further details.

General Procedure of the Hydrosilylation of Olefins

In a vial equipped with a magnetic stir bar, di*iso*propylethylamine (25 mol%) was added to a solution of alkene (100 mol%, 0.5 mmol), phenylsilane (120 mol%), and ^{Et}BIPFe(OTf)$_2$ (**1c**, 2 mol%). The mixture was stirred at room temperature for 1 h. Diethylether was subsequently added. The mixture was passed through a short silica plug to remove the iron species, and the solvent removed *in vacuo* to give the crude product. 1,3,5-trimethoxybenzene was used as an internal standard (20 mol%).

Details on all materials and methods, along with characterization data are available in the Supporting Information.

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References

[1] J. L. Speier, J. A. Webster, G. H. Barnes, *J. Am. Chem. Soc.* **1957**, *79*, 974-979.

[2] B. Marciniec, H. Maciejewski, C. Pietraszuk, P. Pawluc, *Hydrosilylation: A Comprehensive Review on Recent Advances*, (Ed. B. Marciniec) Springer, New York, **2009**.

[3] I. Ojima, *The Hydrosilylation Reaction*, in *Organic Silicon Compounds Volume 1 and Volume 2*, (Eds. S. Patai and Z. Rappoport) John Wiley & Sons, Ltd, Chichester, **1989**.

[4] P. B. Hitchcock, M. F. Lappert, N. J. W. Warhurst, *Angew. Chem. Int. Ed*. **1991**, *30*, 438-440; *Angew. Chem*. **1991**, *103*, 439-441.

[5] I. E. Markó, S. Stérin, O. Buisine, G. Mignani, P. Branlard, B. Tinant, J. P. Declercq, *Science* **2002**, *298*, 204-206.

[6] A. M. Tondreau, C. C. H. Attenza, K. J. Weller, S. A. Nye, K. M. Lewis, J. G. P. Delis, P. J. Chirik, *Science* **2012**, *335*, 567-570.

[7] D. Trogel, J. Stohrer, Coord. *Chem. Rev*. **2011**, *255*, 1440-1459.

[8] P. J. Chirik, Modern Alchemy: *Replacing Precious Metals with Iron in Catalytic Alkene and Carbonyl Hydrogenation Reactions* in *Catalysis without Precious Metals*, (Ed. R. M. Bullock) Wiley-VCH, Weinheim, **2010**, pp. 83-110.

[9] Y. Nakajima, S. Shimada, *RSC Adv*. **2015**, *5*, 20603-20616.

[10] P. J. Chirik, A. M. Tondreau, J. G. P. Delis, K. M. Lewis, K. J. Weller, S. A. Nye (Cornell University, Momentive Performance Materials Inc. USA), US 20120130106, **2012**.

[11] a) S. C. Bart, K. Chlopek, E. Bill, M. W. Bouwkamp, E. Lobkovsky, F. Neese, K. Wieghardt, P. J. Chirik, *J. Am. Chem. Soc*. **2006**, *128*, 13901-13912; b) M. W. Boukamp, A. C. Bowman, E. Lobkovsky, P. J. Chirik, *J. Am. Chem. Soc*., **2006**, *128*, 13340-13341.

[12] S. C. Bart, E. Lobkovsky, P. J. Chirik, *J. Am. Chem. Soc*., **2004**, *126*, 13794-13807.

[13] a) J. Y. Wu, B. N. Stanzl, T. Ritter, *J. Am. Chem. Soc*. **2010**, *132*, 13214-13216; b) C. Belger, B. Plietker, *Chem. Commun*. **2012**, *48*, 5419-5421; c) G. Hilt, P. Bolze, I. Kieltsch, *Chem. Commun*. **2005**, *15*, 1996-1998; d) B. Moreau, J. Y. Wu, T. Ritter, *Org. Lett.* **2009**, *11*, 337-339; e) J. G. P. Delis, S. A. Nye, K. M. Lewis, K. J. Weller, P. J. Chirik, A. M. Tondreau, S. K. Russell (Momentive Performance Materials Inc. USA), US 20110009573 A1, **2011**; f) L. Zhang, D. Peng, X. Leng, Z. Huang, *Angew. Chem*. **2013**, *125*, 3764-3768; *Angew. Chem. Int. Ed*. **2013**, *52*, 3676-3680; g) M. D. Greenhalgh, D. J. Frank, S. P. Thomas, *Adv. Synth. Catal*. **2014**, *356*, 584-590.

[14] a) M. D. Greenhalgh, S. P. Thomas, *J. Am. Chem. Soc*. **2012**, *134*, 11900-11903; b) E. Nakamura, N. Yoshikai, *J. Org. Chem*. **2010**, *75*, 6061-6067.

[15] K. Kamata, A. Suzuki, Y. Nakai, H. Nakazawa, *Organometallics*, **2012**, *31*, 3825-3828.

[16] J. Chen, B. Cheng, M. Cao, Z. Lu, *Angew, Chem. Int. Ed*. **2015**, *54*, 4661-4664; *Angew. Chem*. **2015**, *127*, 4744-4747.

[17] a) A. M. Trzeciak, Z. Ciunik, J. J. Ziolkowski, *Organometallics*, **2002**, *21*, 132-137; b) C. C. Lu, J. C. Peters, *J. Am. Chem. Soc*. **2004**, *126*, 15818-15832; c) G. C. Christoph, V. L. Goedken, *J. Am. Chem. Soc*. **1973**, *95*, 3869-3875; d) C. E. Castro, M. Jamin, W. Yokoyama, R. Wade, *J. Am. Chem. Soc.* **1986**, *108*, 4179-4187; e) A. Meffre, S. Lachaize, C. Gatel, M. Respaud, B. Chaudret, *J. Mater. Chem*. **2011**, *21*, 13464; f) J. D. S. Newman, G. J. Blanchard, *Langmuir*, **2006**, *22*, 5882-5887; g) S. B. Hawkins, J. C. Peters, *Organometallics*, **2002**, *21*, 1753-1755; h) J. Barrera, S. D. Orth, W. D. Harman, *J. Am. Chem. Soc*., **1992**, *114*, 7316-7318.

[18] R. W. Taft, F. G. Bordwell, *Acc. Chem. Res*. **1998**, *21*, 463-469.

[19] M. Á. Cartes, P. Palma, J. J. Sandoval, J. Cámpora, E. Álvarez, *Inorganica Chimica Acta* **2014**, *412*, 73-78.

[20] B. Marciniec, *Coord. Chem. Rev*. **2005**, *249*, 2374-2390.

[21] *Refer to Supporting Information for further details.*

[22] M. S. Singh, S. Chowdhury, *RSC Adv*. **2012**, *2*, 4547-4592.

[23] a) X. Zheng, L. Yang, W. Du, A. Ding, H. Guo, *Chem. Asian J*. **2014**, *9*, 439-442; b) H. Huang, W. Guo, W. Wu, C. J. Li, *Org. Lett.* **2015**, *17*, 2894-2897; c) X. Tang, L. Huang, C. Qi, X. Wu, W. Wu, H. Jiang, *Chem. Commun*. **2013**, *49*, 6102-6104; d) U. C. Yoon, P. S. Mariano, *Acc. Chem. Res*. **1992**, *25*, 233-240.

[24] D. Peng, Y. Zhang, X. Du, L. Zhang, X. Leng, M. D. Walter, Z.Huang *J. Am. Chem. Soc*. **2013**, *135*, 19154-19166.

[25] W. M. Czaplik, S. Grupe, M. Mayer, A. Jacobi von Wangelin, *Chem. Commun.* **2010**, *46*, 6350-6352.

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Amine Activated Iron Catalysis: Air- and Moisture Stable Alkene and Alkyne Hydrofunctionalization

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